Review

Selenium analysis in waters. Part 1: Regulations and standard methods

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HIGHLIGHTS

- Environmental selenium contamination is detrimental to aquatic life.
- Selenium concentrations in many types of waters are strictly regulated.
- Methods to analyze selenium in waters are becoming more sensitive and robust.
- Selenium speciation plays a vital role in its bioavailability to aquatic life.

GRAPHICAL ABSTRACT
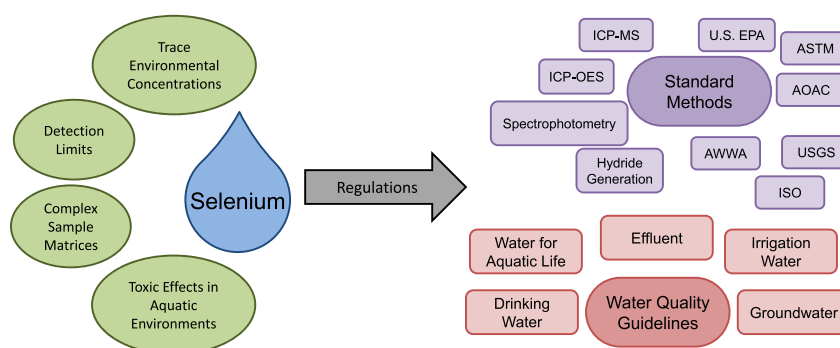
ABSTRACT

Selenium is released into the aquatic environment through anthropogenic activities such as agricultural irrigation, coal mining, and metallurgical activities, where it acts as a reproductive toxin with negative effects on predatory fish and water fowl. Waterborne selenium concentrations are closely regulated worldwide, and various standardized methods are implemented by regulatory bodies to allow for the monitoring of selenium concentrations in different types of waters. Here, we discuss worldwide regulations relating to concentration limits of selenium in drinking, natural, and industrial waters. Focusing specifically on North America, we look at some standardized analysis methods and discuss the fact that many of these methods are not adequately sensitive to measure selenium in the concentrations outlined by the associated regulations for natural waters. We look in detail at the limitations of these methods with regards to both detection limits and interfering sample matrix components and establish the need for more sensitive and robust methods of analysis for regulatory compliance. This review is complemented by a second part (LeBlanc et al., 2018) where we discuss the state of selenium speciation analysis and importance of speciation data for decision makers in industry and regulators.

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1. Introduction

Selenium (Se) is a naturally occurring element, present in the earth's crust with a relative abundance of 0.3 to 10×10^{-6}%, depending on geographical region (Fleischer, 1953), which is mobilized through various anthropogenic activities. Over the last several decades, interest in Se has increased significantly, particularly in North America, due to its severe impact on aquatic ecosystems (Hamilton, 2004; Lemly, 2002a, 2007). As a result, regulations controlling maximum permissible Se concentrations in drinking waters, industrial effluents, and natural surface waters have become increasingly stringent, which has posed challenges to analysts measuring Se in these types of samples. In this review, we discuss these challenges in terms of the regulations/guidance by various governmental and non-governmental bodies and outline the analytical methods accepted by these regulators. We then critically examine the outcomes of such methods and discuss challenges that will likely be faced in the future of Se analysis, specifically in terms of the achievable detection limits and interfering sample matrix components, establishing the need for more sensitive and robust methods of analysis for regulatory compliance. In Part 2 of this review (LeBlanc et al., 2018), we expand this discussion to examine the state of Se speciation analysis and importance of speciation data for decision makers in industry and regulators.

2. Selenium in the environment

2.1. Occurrence, production and uses of selenium

The United States Geological Survey (USGS) Mineral Commodity Profiles of Se estimated its production was approximately 2200–2300 t between 2013 and 2016, with the largest producers including the United States, Canada, Peru, the European Union (EU), Russia, China, and Japan (United States Geological Survey, 2018). Se is classified as economic minor metal and it is produced and sold in the form of pure SeO_2 powder (>99%) and Se ingot. Se is used in variety industries, as illustrated in Fig. 1.

Among the "other uses" of Se are pharmaceuticals, cosmetics (though selenium sulfide is prohibited, except in anti-dandruff shampoos where its limited quantity is labelled (European Parliament and of the Council on Cosmetic Products, 2009)), and food and feed additives (Yukon Zinc Corporation, 2005).

While Se has been classified as a non-metal (Rumble, 2016), environmental chemists typically consider it to be a metalloid due to its chemical behaviour. In naturally-occurring minerals, Se often coexists with iron, lead, zinc, cadmium, copper, or silver, but upon mobilization via contact with water Se forms the soluble oxyanions of selenite (Se (IV)) and/or selenate (Se(VI)) at the different pH and redox conditions (Eh) shown in Fig. 2 (Howard, 1977). Se in the water column can also be present in two additional oxidation states: elemental Se^0, and Se^{2-} (selenide) which is typically found as an organic Se species such as selenomethionine (SeMet) or selenocysteine (SeCys) (Maher et al., 2010).

Background concentrations of Se in uncontaminated surface waters are generally below 1 µg/L (Seiler et al., 1965), but in areas where the weathering and erosion of seleniferous soils is augmented by anthropogenic activities such as agricultural irrigation, environmental Se concentrations have been shown to be significantly elevated. For example, early studies of the San Joaquin Valley region noted Se concentrations up to 100 mg/kg in the sediments of evaporation ponds (Dungan and Frankenberger, 1999; Saiki and Lowe, 1987). Other anthropogenic activities known to mobilize Se include petroleum refining, certain mining operations (e.g. Cd and Zn), and the combustion of fossil fuels. In particular, coal mined from high-sulfur areas such as the southeastern United
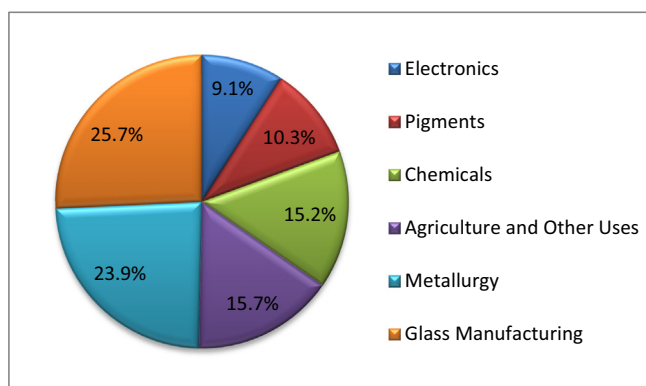
Fig. 1. World consumption of selenium.
Adapted from Yukon Zinc Corporation (2005)

States contains elevated levels of Se, which is released via vapor- and particulate-phase emissions as SeO_3 or trapped along with sulfur in flue gas desulfurization (FGD) waters, producing a Se-contaminated wastewater that must be treated before release back into the environment (Electric Power Research Institute, 2008; Maher et al., 2010).

2.2. Selenium contamination in aquatic environments – the issue and proposed regulations

While it has been demonstrated that 0.1–0.3 mg/kg Se in the diet is generally nutritionally adequate (Mayland, 1994), elevated intake is cause for significant concern, particularly in oviparous animals such as predatory fish and waterfowl where it results in teratogenic effects that can affect entire populations in contaminated ecosystems (Janz et al., 2010). However, one of the most significant challenges being faced by those attempting to manage environmental Se toxicity lies in the fact that there is no apparent correlation between the total Se concentration in a water body and the associated effects observed in the animal population within that ecosystem. These inconsistencies arise from the mechanisms by which Se enters the aquatic food web, where the majority of the bioconcentration occurs between the water and the

lowest trophic level (usually algae). The extent of this bioconcentration varies over several orders of magnitude and is dependent on both the species of algae and the species of Se present in the water (Baines and Fisher, 2011). For example, the algal uptake of the organic Se species SeMet has been shown to occur much more quickly and to a greater extent than the uptake of Se(IV) or Se(VI) (Besser et al., 1989; Riedel et al., 1991; Sandholm et al., 1973). Additionally, inhibitory effects on the uptake of Se(IV) and Se(VI) by algae have been observed in the presence of phosphate and sulfate, respectively (Riedel and Sanders, 1996).

Due to this inconsistency between waterborne Se concentration and observed toxic effects, the United States Environmental Protection Agency (U.S. EPA) has recently released new guidelines for Se in the environment which consider fish egg/ovary Se as the primary indicator when examining a body of water, rather than looking at the water column concentration alone, as has been done historically (U.S. EPA, 2016). This type of monitoring and regulation can provide a better indication of Se's effects as a reproductive toxin than whole-body or muscle-based concentrations (Hamilton, 2002), although those values are to be monitored when egg/ovary concentrations are not available (U.S. EPA, 2016) because they are still more relevant than water column concentrations (Hamilton, 2002), which are used as a last resort (U.S. EPA, 2016).

2.3. Selenium toxicity to humans

Se is an essential micro nutrient element at low levels, but toxic when an excessive amount is consumed. Generally, humans intake Se through their diet, though the amount of Se in food varies globally depending on soil geology (Kunli et al., 2004). The recommended dietary allowance of Se established by the U.S. Agency for Toxic Substances and Disease Registry is 55 μg/day for adults (Agency for Toxic Substances and Disease Registry, 2003). The International Agency for Research on Cancer (IACR) has reviewed many research studies on the relationship between Se and cancers in humans and other animals and concluded that there is inadequate evidence to classify Se as a carcinogen (World Health Organization, 1975).

Incidences of Se poisoning in humans are rare. Acute toxicity has been reported as both intentional and, more commonly, accidental intake of inorganic Se. The symptoms of acute toxicity include strong garlic-like odours from patients' breath, vomiting, abdominal pain, and diarrhea. High concentrations of Se were found in the blood, liver, kidney, and heart of patients (Nuttall, 2006). Toxic effects caused by the inhalation of Se were reported in the chemical manufacturing industry, when a man was exposed to Se fumes from the reaction of selenic acid with caustic soda. The man died as a result of second-degree skin burns, necrosis of oral mucous membranes, and hemorrhagic lung edema; a post-mortem examination revealed high concentrations of Se in the victim's blood serum, urine, stomach contents, and lungs (Schellmann et al., 1986).

In 2008, there were reports of a misformulated supplementary product reaching the U.S. commercial market, where the actual Se content of a product was 200 times the labelled concentration (MacFarquhar et al., 2010; National Institutes of Health, 2018). While no fatal cases were reported, symptom of acute Se poisoning occurred within two weeks. Many patients developed gastrointestinal symptoms (nausea, vomiting, diarrhea, abdominal pain) and musculoskeletal effects (muscle pain, joint pain, cramps). Some patients also reported hair loss, and nail discoloration and brittleness. To follow up, monitoring Se levels in the body was conducted via urine, hair, nail, and serum analysis (MacFarquhar et al., 2010). The chronic effects of long term Se consumption are known as selenosis, and include the development of brittle hair and deformed nails, and the impairment of the synthesis of thyroid and growth hormones. In the most extreme cases, neurotoxicological effects may develop resulting in the loss of feeling and control of the arms and legs (Vinceti et al., 2001).
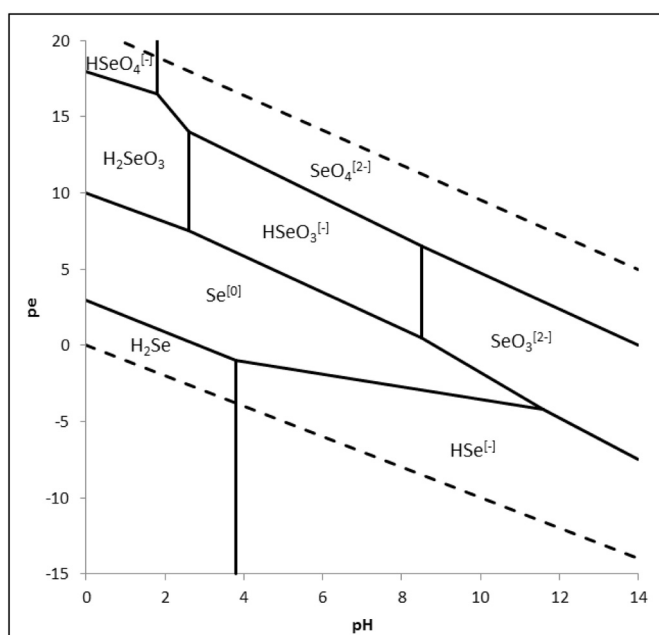

Fig. 2. pe-pH diagram for Se at 25 °C and 1 bar, when $I = 0$; based on Séby et al. (2001).

3. Water quality guidelines for selenium

Se and Se-containing compounds are classified by the International Agency for Research on Cancer (IARC) as "unclassifiable as to carcinogenicity in humans" (World Health Organization, 1975). Se is of concern in the areas of seleniferous soils from which Se could accumulate in plants and livestock and become released to aquatic environment. Seleniferous soils are present in many areas of the world such as in North America: Great Plains of the U.S. and Canada; in South America: Chili, Venezuela; in Asia: Enshi County Hubei Province China, northwestern India, and Turkey; in Europe: Denmark, Norway, Finland, Sweden, Poland, Germany, Ireland, Spain, and Greece; and parts of Australia and New Zealand (Comb, 2001; Dhillon and Dhillon, 2014; Oldfield, 2002; Sasmaz et al., 2015).

Due to the evidence showing the detrimental effects of Se on aquatic life (Hamilton and Buhl, 2003; Hume, 2014; May et al., 2008; Muscatello et al., 2008), the maximum permissible concentration of Se in habitat waters is, on average, 10 times lower than that in drinking water, at values of 1–5 μg/L and 10–50 μg/L, respectively (Lemly, 2007). While overall, these guidelines for Se in freshwater for aquatic life are very low level, they do vary from country-to-country. The Se toxicity criteria for aquatic life (fish and birds) is a controversial issue because there are several factors involved such as vulnerable aquatic life species, type of water (lentic and lotic water), water temperature, fish diet source, age of aquatic animals and other co-contaminants (Lemly, 2007).

This section describes Se concentration limits proposed by national and international bodies for drinking water, water intended for (human) consumption, fresh water for irrigation, for livestock and for aquatic life, effluents, and marine water. The guidelines for Se outlined in Table 1 are organized by country or region and are divided into drinking water, groundwater, marine water, water supplies for communities, effluent discharged into waterways, and waters with various intended uses including recreation, irrigation, livestock watering, and for protection of aquatic life.

3.1. World Health Organization water quality guidelines

In 1958, the World Health Organization (WHO) established the International standard for drinking water after a questionnaire had circulated among members of the WHO in 1953 and revealed a problem and the need for standard criteria for water quality. As a minimum requirement, drinking water for human consumption must be physically accepted as free from chemical substances and micro-organisms. The first edition of "WHO - Standard Drinking Water Quality" identified and regulated a few toxic substances: arsenic, chromium, lead, Se and cyanide (World Health Organization, 1958). Five years later, the second edition of "WHO - Standard Drinking Water Quality" was published with more stringent regulations of maximum allowable concentrations of toxic substances, including Se where the allowable limit was decreased from 50 μg/L to 10 μg/L, and also added barium and cadmium into the list of toxic substances (World Health Organization, 1963).

The chemical and physical requirements for water were classified into four groups including: (1) toxic chemical substances, (2) specific chemicals which may affect health, (3) chemicals affecting the potability of water, and (4) chemical and physical indicators of pollution (World Health Organization, 1958, 2011b). Among these classifications, Se falls into the toxic chemical substances category, with the maximum allowable limit closely regulated. Later in "WHO - Guideline for Standard Drinking Water Quality" (2011b, 4th Edition), the chemical substances requirement categories were further classified according to source categories including: 1) natural occurring chemicals, 2) chemicals from industrial sources and human dwellings, 3) chemicals from agricultural activities, and 4) chemicals used in water treatment or from materials in contact with drinking water. The presence of any of these substances in excess of the allowable concentrations results in the water being prohibited in use as a public supply. In WHO – 2011, Se is classified as a "naturally occurring chemical" (World Health Organization, 2011b).

Se concentrations in drinking water of "WHO – 1st Edition" in 1958 were set at 50 μg/L, which was revised to 10 μg/L in "WHO – 2nd Edition" in 1963. The current "WHO – 4th Edition, Standard for Drinking Water Quality", Se has been revised again to 40 μg/L. The limit of Se in drinking water was calculated using an average total daily intake (TDI of 0.005 mg/kg/day (Canadian International Development Agency, 2017) or 400 μg/day/man (World Health Organization, 2011a)) of water consumed per day, by an adult male (average weight of 70 kg) and a fraction of the TDI allocated to drinking-water (20% of TDI). The upper tolerable level of Se at 400 μg per day is recommended by The Food and Agricultural Organization (FAO)/the WHO expert consultation meeting in Bangkok in 1998, and the United Kingdom Expert Group on Vitamins and Minerals (EGVM) (World Health Organization, 2011b). However this guideline for Se may be modified according to variable factors such as the weight of the average adult, and the fraction (%) of the TDI represented by Se intake from the diet. While these factors vary by country and/or geographical region, where these factors are not known, the WHO guideline may be considered (World Health Organization, 2011b).

3.2. North American water quality guidelines

Preliminary surveys of Se (to establish the background data) were conducted on soil, plant, and water samples from areas in the U.S. Great Plains during the period 1928–1933 (Durrell and Cross, 1944; Lambert, 1947). The survey of water in South Dakota, found 8% of the 586 samples collected from seleniferous regions had Se concentrations exceeding 10 μg/L (Stach, 1978). The U.S. Public Health Service (U.S. PHS) first developed the drinking water standard in 1946 and Se was regulated at a concentration limit of 50 μg/L. In 1962, the U.S. PHS revised the maximum limit of Se in drinking water to 10 μg/L (Department of Health Education and Welfare, 1962; Write, 1962).

In 1972, U.S. Federal Government enforced requirements under the Clean Water Act (CWA) regulating the discharge of pollutants into waters as well as quality standards for surface waters, and the Safe Drinking Water Act (SDWA) to regulate the quality of drinking water. The regulations on water quality are mentioned in 40 CFR Part 131 - Water quality standard, Part 132 - Water quality guidance for the great lake system, Part 141 - National primary drinking water, and 40 CFR Part 264 - Standard for owners and operators of hazardous, waste treatment, storage and disposal facilities. In Canada, drinking water standard guidelines are the responsibility of Health Canada, and natural water quality and aquatic system guidelines across Canada are under the control of the Environment and Climate Change of Canada (ECCC) and the individual provinces.

Both the U.S. and Canada regulate the maximum limit of Se in drinking water at 50 μg/L as a minimum requirement. However states/provinces can modify the value to satisfy their needs, as long as the value is not greater than that imposed by the Federal Government's requirement. Many states in the U.S. and provinces in Canada have revised the Se maximum allowable limit to 10 μg/L, as seen in Table 1.

Researchers in the U.S. and Canada have conducted many studies on the toxicity of Se to aquatic fish and birds (Hamilton and Buhl, 2003; Hume, 2016; May et al., 2008). The U.S. and Canada have established the concentration limit of Se in fresh water to protect aquatic life at the low level of 1 to 5 μg/L (see Table 1). The low limit of Se in freshwater is set according to the chronic effect of Se in water column to vulnerable aquatic habitats. Many protocols for assessing the toxicity of Se use models to calculate the daily allowable intake of Se in aquatic habitats and therefore the safe total maximum daily loads for mining effluents, based on data proposed by many researchers (Lemly, 1995, 2002b; Peterson and Nebeker, 1992).

Recently, oil sands, coal, metal and mineral mining in Canada have been in the focus of much attention, as a result of proposed, new more

Table 1
Waters quality guidelines for selenium.

Matrix	Limit (μg/L)	Country or organization	Reference
Drinking water	10	Canada:	
		British Columbia	(British Columbia Ministry of Environment, 2017b)
		Ontario	(Ontario Minsitry of the Environment, 2002)
		Quebec	(Government of Québec, 2017)
		Saskatchewan	(Government of Saskatchewan, 2002)
		New Brunswick	(Government of New Brunswick, 2018)
		United States:	
		Oklahoma	(Oklahoma Administrative Code, 2016)
		Australia	(Australian National Health and Medical Research Council and Australian National Resource Management Ministerial Council, 2016)
		Brazil	(Brazilian Ministry of the Environment, 2012)
		China	(Ministry of Health of China, 2006)
		European Union	(The European Parliament and the Council of the European Union, 1998)
		Germany	(Bartel, 2007)
		Ireland	(Hayes et al., 2012)
		Japan	(Japan Ministry of Health Labour and Welfare, 2004)
		India	(Bureau of Indian Standards, 1991)
		Malaysia	(Ministry of Health Malaysia, 2010)
		Mexico	(Martell et al., 2016)
		Poland	(Polish Ministry of Health, 2010)
		Russia	(Ministry of Health of Russia, 2002)
		Singapore	(National Environment Agency Singapore, 2008)
		United Kingdom	(Government of the United Kingdom, 2016)
		Thailand	(Ministry of Industry Thailand, 1968)
Drinking water	40	World Health Organization	(World Health Organization, 2011b)
		Abu Dhabi	(The Regulation and Supervision Bureau for the water wastewater and electricity sector in the Emirate of Abu Dhabi, 2014)
Drinking water	50	Canada:	
		Federal Government	(Health Canada, 2017)
		Alberta	(Government of Alberta, 2016)
		Newfoundland and Labrador	(Newfoundland Department of Environment and Conservation, 2013)
		Nova Scotia	(Province of Nova Scotia, 2017)
		Prince Edward Island	(Government of Prince Edward Island, 2015)
		Yukon	(Commission of Yukon, 2007)
		United States:	
		U.S. EPA	(U.S. EPA, 2009)
		Arizona	(Arizona Department of Environmental Quality, 2009)
		California	(Government of California, 2017)
		Colorado	(Colorado Department of Public Health and Environment, 2005)
		Kansas	(Kansas Department of Health and Environment, 2017)
		Minnesota	(Minnesota Pollution Control Agency, 2017)
		Missouri	(Missouri Department of Natural Resources, 2015)
		Montana	(Montana Department of Environmental Quality, 2015)
		Nevada	(Nevada Administrative Code, 2016)
		North Dakota	(North Dakota Centruy Code, 2001)
		Nebraska	(Nebraska Department of Environmental Quality, 2015)
		New Mexico	(New Mexico Administrative Code, 2013)
		South Carolina	(South Carolina Department of Health and Environmental Control, 2014)
		Tennessee	(Tennessee Department of Environment and Conservation, 2008)
		Texas	(Texas Commission on Environmental Quality, 2014)
		West Virginia	(West Virginia Department of Environmental Protection, 2015)
		Wisconsin	(Wisconsin Department of Natural Resources, 2017)
		Wyoming	(Wyoming Department of Environmental Quality, 2016)
		South Africa	(Department of Water Affairs and Forestry, 1996b)
		Tanzania	(Energy and Water Utilities Regulatory Authority of Tanzania, 2014)
Water for human consumption	20	South Africa	(Department of Water Affairs and Forestry, 1996a)
Water for human consumption	120	United States:	
		Oregon	(Oregon Department of Environmental Quality, 2011)
Water for human consumption	170	United States:	
		Idaho	(Idaho Department of Environmental Quality, 2011)
		Iowa	(Iowa Department of Natural Resources, 2017)

Table 1 (*continued*)

Matrix	Limit (µg/L)	Country or organization	Reference
		Vermont	(Vermont Department of Environmental Conservation, 2014)
		Virginia	(Virginia State Water Control Board, 2011)
Natural mineral water	10	Codex	(Codex Alimentarius, 2001)
Water for livestock	20	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000)
Water for livestock	30	Canada: British Columbia	(British Columbia Ministry of Environment, 2017a)
Water for livestock	50	Canada: Federal Government	(Canadian Council of Minister of the Environment, 2017)
		Ontario	(Ontario Ministry of the Environment, 1994)
		United States: Arizona	(Arizona Department of Environmental Quality, 2009)
		Nevada	(Nevada Administrative Code, 2016)
		Brazil	(Brazilian Ministry of the Environment, 2012)
		South Africa	(Department of Water Affairs and Forestry, 1996a)
Water for irrigation	10	Canada: British Columbia	(British Columbia Ministry of Environment, 2017a)
Water for irrigation	20	Canada: Alberta	(Government of Alberta, 2016)
		Ontario	(Ontario Ministry of the Environment, 2011)
		United States: Arizona	(Arizona Department of Environmental Quality, 2009)
		Colorado	(Colorado Department of Public Health and Environment, 2005)
		Nebraska	(Nebraska Department of Environmental Quality, 2015)
		Nevada	(Nevada Administrative Code, 2016)
		South Africa	(Department of Water Affairs and Forestry, 1996a)
		United Nations Food and Agriculture Organization	(Ayers and Westcot, 1994)
Water for irrigation	50	United States: Utah	(Utah Administrative Code, 2017)
Water for irrigation (long term, 100 years)	20	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000)
Water for irrigation (short term, 20 years)	50	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000)
Water for irrigation (intermittent)	50	Canada: Federal Government	(Canadian Council of Minister of the Environment, 2017)
Fresh water for aquatic life	1	Canada: Federal Government	(Canadian Council of Ministers of the Environment, 2017)
		Alberta	(Alberta Environment and Sustainable Resource Development, 2014)
Fresh water for aquatic life	2	Canada: British Columbia	(British Columbia Ministry of Environment, 2017a)
		United States: Arizona	(Arizona Department of Environmental Quality, 2009)
		South Africa	(Department of Water Affairs and Forestry, 1996b)
Fresh water for aquatic life	4.6	United States: Colorado	(Colorado Department of Public Health and Environment, 2005)
		Pennsylvania	(Pennsylvania Code, 2012)
		Utah	(Utah Administrative Code, 2017)
Fresh water for aquatic life	5	United States: Alabama	(Alabama Department of Environmental Management, 2017)
		Florida	(Florida Administrative Code, 2015)
		Georgia	(Georgia Department of Natural Resources, 2016)
		Maine	(Maine Department of Environmental Protection, 2005)
		Nebraska	(Nebraska Department of Environmental Quality, 2015)
		New Hampshire	(New Hampshire Code of Administrative Rules, 2015)
		North Carolina	(North Carolina Department of Environment and Natural Resources, 2007)
		North Dakota	(North Dakota Century Code, 2001)
		South Carolina	(South Carolina Department of Health and Environmental Control, 2014)
		South Dakota	(South Dakota Legislative Research Council, 1999)
		Virginia	(Virginia State Water Control Board, 2011)
		Tennessee	(Tennessee Department of Environment and Conservation, 2008)
		Vermont	(Vermont Department of Environmental Conservation, 2014)

Table 1 (*continued*)

Matrix	Limit (μg/L)	Country or organization	Reference
		Washington	(Washington State Legislature, 2016)
		West Virginia	(West Virginia Department of Environmental Protection, 2015)
Fresh water for aquatic life	10	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000)
Fresh water for aquatic life	35	United States: Oregon	(Oregon Department of Environmental Quality, 2011)
Fresh water for aquatic life	100	Canada: Ontario	(Ontario Ministry of the Environment, 1994)
Fresh water	3	Germany	(Irmer and Blondzik, 2014)
Fresh water (lentic, chronic 30 day)	1.5	United States: U.S. EPA	(U.S. EPA, 2016)
Fresh water (lotic, chronic 30 day)	3.1	United States: U.S. EPA	(U.S. EPA, 2016)
Fresh water (continuous concentration)	5	United States: U.S. EPA	(U.S. EPA, 2016)
Surface water	10	Ireland	(Hayes et al., 2012)
		Bulgaria	(Stoimenova et al., 1998)
		Romania	(Popovici et al., 1998)
Marine water	10	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000)
		Brazil	(Brazilian Ministry of the Environment, 2012)
Marine water (chronic)	71	United States: U.S. EPA	(U.S. EPA, 2017d)
Groundwater	1	Canada: British Columbia	(British Columbia Ministry of Environment, 2017b)
Groundwater	10	Brazil	(Brazilian Ministry of the Environment, 2012)
		Japan	(Japan Ministry of the Environment)
		Thailand	(Thailand Ministry of Industry, 1978)
Groundwater	50	Canada: Alberta	(Government of Alberta, 2016)
		Newfoundland and Labrador	(Water Resources Management Division, 2009)
Groundwater (full depth background site condition standards)	5	Canada: Ontario	(Ontario Ministry of the Environment, 2011)
Groundwater; generic site, full depth generic and stratified site condition standards in a potable groundwater condition, and generic site condition standards for use within 30 m of a water body in a potable groundwater condition	10	Canada: Ontario	(Ontario Ministry of the Environment, 2011)
Groundwater; generic site condition standards for shallow soils in a non-potable groundwater condition and generic site condition standards for use within 30 m of a water body in a non-potable groundwater condition	50	Canada: Ontario	(Ontario Ministry of the Environment, 2011)
Groundwater (full depth generic and Stratified site condition standards in a non-potable groundwater condition)	63	Canada: Ontario	(Ontario Ministry of the Environment, 2011)
Groundwater for livestock	10	Brazil	(Brazilian Ministry of the Environment, 2012)
Groundwater for irrigation	50	Brazil	(Brazilian Ministry of the Environment, 2012)
Effluent	20	Thailand	(Thailand Ministry of Science Technology and Environment, 1996)
Effluent	50	India	(Bureau of Indian Standards, 1981; Thailand Ministry of Industry, 1996)
Effluent	300	Brazil	(Brazilian Ministry of the Environment, 2012)
Effluent	100	United Nations World Bank Group United States: Florida	(The World Bank Group, 1999) (Florida Department of State, 2014)
Effluent	500	Singapore	(National Environment Agency of Singapore, 2017)
Effluent into controlled water	10	Singapore	(National Environment Agency of Singapore, 2017)
Effluent into controlled water	20	Thailand	(Thailand Ministry of Industry, 1996)
Effluent into groundwater	20	United States: New York	(New York Department of State-Division of Administrative Rules, 2016)
Effluent into harbor and irrigation	20	Dubai	(Government of Dubai, 2013)
Effluent into the environment or to storm sewers	50	Canada: Newfoundland and Labrador	(Ryan, 2003)
Effluent into coastal	50	India	(Bureau of Indian Standards, 1981)
Effluent into municipal or industrial effluent treatment	100	Canada: Newfoundland and Labrador	(Ryan, 2003)
Effluent into seawater (instantaneous)	150	United States: California	(California State Water Resources Control Board, 2015)

Table 2
Isobaric and polyatomic interferences for selenium analysis by ICP-MS.

Se isotope	Isotope abundance (%)	Isobaric interferences	Polyatomic interferences	Recommended mass referenced by
^{74}Se	0.87	^{74}Ge	$^{37}Cl_2^+$, $^{36}Ar^{38}Ar^+$, $^{38}Ar^{36}S^+$, $^{40}Ar^{34}S^+$	
^{76}Se	9.02	^{76}Ge	$^{40}Ar^{36}Ar^+$, $^{40}Ar^{36}S$	
^{77}Se	7.58	$^{154}Gd^{2+}$	$^{36}Ar\,^{40}Ar^1H^+$, $^{38}Ar_2^1H^+$, $^{40}Ar^{37}Cl^+$, $^{12}C^{19}F^{14}N^{16}O_2^+$	AOAC 993.14, APHA 3125B, ISO 17294-1 (for low Cl$^-$)
^{78}Se	23.52	$^{78}Kr^+$, $^{156}Gd^{2+}$	$^{40}Ar^{38}Ar^+$, $^{38}Ar^{40}Ca^+$	USGS, (Garbarino, 1999) ISO 17294-1 (for high Cl and Br)
^{80}Se	49.82	$^{80}Kr^+$, $^{160}Gd^{2+}$	$^{40}Ar_2^+$, $^{40}Ar^{40}Ca^+$, $^{32}S^{16}O_3^+$	AOAC 993.14
^{82}Se	9.19	$^{82}Kr^+$	$^{40}Ar_2^1H^+$, $^{40}Ar_2^1H_2^+$, $^{81}Br^1H^+$, $^{12}C^{35}Cl_2^+$, $^{34}S^{16}O_3^+$	EPA 200.8 (must be monitored), APHA 3125B, USGS, ISO 17294-1 (for low Br), ASTM D5673

stringent regulations for Se in discharge waters from mining operations. In a consultation document issued by Environment and Climate Change Canada (ECCC), it is being recommended that Se be monitored and controlled in mining permits through proposed Amendments to the Metal Mining Effluent Regulations (MMER) (Government of Canada, 2017). MMER were initially promulgated in 2002 under Canada's Fisheries Act, which prohibits the deposit of deleterious substances into fish frequented waters unless authorized by regulations. The MMER currently require metal mines to monitor the concentration of selenium in their effluent as part of the Effluent Characterization provisions of the Environmental Effects Monitoring requirements. This obligates metal mines to report on hardness, alkalinity, electrical conductivity and temperature of effluent water samples, and also on the concentrations, in total values, of aluminum, iron, mercury, molybdenum, selenium, ammonia and nitrate. In addition to metal mines, the proposed Amendments to MMER would extend regulatory controls to diamond mining and potentially coal mines, and would also expand the list of substances monitored to include chloride, chromium, cobalt, sulfate, thallium, uranium, phosphorous and manganese. Additionally, the proposed Amendments would also add mandatory fish tissue study for Se, if the annual average of the concentrations reported under the Effluent Characterization is equal to or >5 μg/L or if any single grab or composite sample is equal to or >10 μg/L.

The United States Environment Protection Agency (U.S. EPA) limits the level of Se in effluent at point source in specific industries, including inorganic chemicals (40 CFR Part 415), waste treatment (40 CFR Part 437), steam electric power generation (40 CFR Part 423) and waste combustors (40 CFR 444). Furthermore U.S. EPA has strictly controlled limits for Se in a variety of water resources and a database of Se background concentrations in soils and waters of specific geological areas; these values are available from the USGS (United States Geological Survey, 2017).

The U.S. EPA has recently released a new "Aquatic Life Ambient Water Quality Criterion for Selenium" (U.S. EPA, 2016). These new regulations not only examine water-column Se, as has been historically monitored, but also use fish tissue Se concentrations to determine whether an ecosystem is contaminated. Since Se is a reproductive toxin, the primary factor considered is the egg/ovary Se, which is not to exceed 15.1 mg/kg (dry weight) at any given time of measurement. When egg/ovary Se is not (or cannot be) monitored, fish whole body or muscle tissue values are used and cannot exceed 8.5 mg/kg or 11.3 mg/kg (dry weight), respectively. Water column Se criteria differ depending on the ecosystem, with average monthly exposure not to exceed 1.5 μg/L in lentic (standing) or 3.1 μg/L in lotic (flowing) waters more than once in a three year period. Intermittent Se water concentration limits are not given as specific values, but are calculated based on the system, as follows:

$$WQC_{int} = \frac{WQC_{30\ day} - c_{bkg}(1 - f_{int})}{f_{int}} \tag{1}$$

where WQC_{int} is the intermittent exposure criterion, WQC_{30day} is the water column monthly exposure criterion for either lentic (1.5 μg/L) or lotic (3.1 μg/L), C_{bkg} is the average background Se concentration, and f_{int} is the fraction of a 30-day period during which Se concentrations are elevated ($f_{int} \geq 0.033$; for 1 day) (U.S. EPA, 2016).

To complicate matters, the areas of concern relating to environmental Se contamination are typically those that involve the release of Se into aquatic ecosystems, usually as (treated) wastewaters. The U.S. EPA regulations account for these scenarios, classifying them as "new inputs" to acknowledge that higher concentrations in both fish tissue and in the water column will be observed until a quasi-steady-state is reached; this may take several months (lotic system) to several years (lentic systems). In these systems, fish-tissue Se concentrations do not take priority over water column concentrations as is the case in general, but instead rely on site-specific criteria (U.S. EPA, 2016).

Table 3
Examples of commercial certified reference materials for Se in water.

Material	Producer	Matrix/sample type	Certified Se concentration
SRM 1640a	National Institute of Standards & Technology	Trace elements in natural water	20.13 + 0.17 μg/L
SRM 1643f	National Institute of Standards & Technology	Trace elements in (pure) water	11.700 + 0.081 μg/L
CRM 7202-b	National Metrology Institute of Japan	Trace elements in river water (elevated level)	1.00 + 0.06 μg/kg
MX014	National Metrology Institute of Australia	Trace elements in sea water	3.17 + 0.28 μg/L
ERM-CA011	European Reference Materials	Hard drinking water - metals	11.13 + 0.47 μg/L
ERM-CA713	European Reference Materials	Wastewater – trace elements	4.9 + 1.1 μg/L
NWTM-35 TM-35	Environment and Climate Change Canada	Lake Ontario water (fortified)	4.60 ± 0.76 μg/L
TMDA-51.5	Environment and Climate Change Canada	Lake Ontario water (fortified)	14.4 + 2.2 μg/L
TM-DWS.3	Environment and Climate Change Canada	Lake Ontario water (fortified)	9.20 + 1.17 μg/L
SPS-SW1	Spectrapure Standards-Norway	Trace elements in surface water	2.0 + 0.02 μg/L
SPS SW2	Spectrapure Standards-Norway	Trace elements in surface water	10.0 + 0.05 μg/L

Table 4
Standard method details and quality control criteria for drinking water, waters and wastewater.

Method	Standard method	Digestion method for each Se fraction	IDL-Se	MDL or LOQ-Se	Method performance indicators to be reported	Reference
HG-AAS (batch)	ASTM D3859-A (Se only)	Dissolved: - Filter sample (0.45 µm) - Process filtrate as total recoverable fraction Total recoverable: - 50 mL sample without filtration - Add methyl orange, 0.5 mL CaCl$_2$ (3% w/v), 0.5 mL HCl (1% v/v), and 3 drops KMnO$_4$ - Boil, evaporate to 25 mL, add 2 mL NaOH (0.4% w/v) - Heat until dryness, cool, add 15 mL HCl, heat for 20 min, cool, add HCl (50% v/v) to make 50 mL - Analyze	No data	No data	Working range: 1–20 µg/L Accuracy and precision: - Overall precision: 0.146X + 0.49 (X = Se concentration) - Reagent water: bias 93 to 106% at 3 to 17 µg/L - Sample: bias 90 to 108% at 3 to 17 µg/L Demonstration of capability: - 7 replicates of standard solution with matrix matching solution at mid-point - Criteria as above for precision and bias for % recovery and STDEV Quality control: - Calibration curve: ≥6 calibration points - IPC at midpoint of calibration curve, 85–115% accuracy - CCB analyzed between every sample set[a] - CCV every 10%, 85–115% accuracy - Reagent blank <1/2 of the lowest calibration concentration - LCS at midpoint calibration 85–115% accuracy - Matrix spike, once per sample set - Matrix spike duplicate n = 1/batch - Use independent reference material	(ASTM International, 2008) (ASTM International, 2012a) (ASTM International, 2015)
HG-AAS	EPA 7741A (Se only)	Total recoverable: - 50 mL sample, add 10 mL HNO$_3$ and 12 mL H$_2$SO$_4$ - Heat until white fumes produced, cool - Add 25 mL DIW, heat until white fumes produced, add H$_2$O and evaporate until observing SO$_3$ fumes are observed, cool - Add 40 mL HCl and make up to 100 mL with DIW	No Data	2 µg/L	Accuracy and precision: - Recovery at 5, 10 and 15 µg/L 100–101% - RSD: 0.6–2.9% Quality control: - IDL evaluation - Participation in proficiency testing - One method blank/batch (<10% of LOQ) - One LCS/batch (measured within ±20% of true value) - Duplicate sample or duplicate spike sample (within 20% RPD) - Post digestion spike addition (within ±20% of spiked value) - 1:5 dilution is within 10% of original determination - Where sample matrix is complex, one point or 3 point standard addition is recommended	(U.S. EPA, 1994b)
STPGF-AAS	EPA 200.9 (Se only)	Direct analysis: - Acid preserved sample with turbidity <1 NTU Dissolved: - ≥20 mL of filtered sample - Add HNO$_3$ to obtain 1% (v/v) - 0.015 mg Pd + 0.01 mg Mg(NO$_3$)$_2$ and 5% H$_2$ (g)/Ar (g) at dry and char step (300 mL/min) Total-recoverable:		0.6 µg/L with EDL	Demonstration of capability: - MDL - Linear dynamic range Quality control: - Calibration curve >6 points - QCS before sample analysis, 90–110% accuracy - Standard solution at concentration 20xIDL - ≥5 replicates, RSD <5% - One LRB every 20 samples (LRB ≤ MDL) - One LFB per batch, 85–115% recovery	(U.S. EPA, 1994a)

Table 4 (*continued*)

Method	Standard method	Digestion method for each Se fraction	IDL-Se	MDL or LOQ-Se	Method performance indicators to be reported	Reference
					- IPC every 10 samples and at the end of sample run, 90–110% accuracy - CB after calibration (<IDL) - LFM every 10% of samples 70–130% recovery	
		- 100 mL sample without filtration - Add 1 mL HNO_3 and 0.5 mL HCl - Heat at 85 °C until volume reaches 20 mL - Gently reflux 30 min - Cool and dilute to 50 mL				
GF-AAS	ASTM D3859-B (Se only)	Dissolved: - Filter sample (0.45 μm) - Add 2 mg $NiNO_3$ and inject sample Total-recoverable: - 100 mL sample without filtration - Add 5 mL H_2O_2 and 5 mL HNO_3 - Heat at 95 °C until volume reaches 15 to 20 mL, cool and filter (0.45 μm)	No data	No data	Working range: 2–100 μg/L Accuracy and precision: - Reagent water overall precision: 0.1072X + 0.54 (X = Se concentration) - Reagent water bias: 85–90% at 3 to 14 μg/L - Sample overall precision: 0.2658X − 0.03 - Sample bias: 76–93% at 3 to 14 μg/L Demonstration of capability: See ASTM D3859-A Quality control - Calibration curve ≥3 points - Instrument check at midpoint of calibration curve, 85–115% accuracy - CCB, CCV between each sample set; 85–115% accuracy on CCV - Reagent blank <1/2 of the lowest calibration concentration - LCS at a midpoint of calibration curve, 85–115% accuracy - Recovery for matrix spike and matrix spike duplicate: see ASTM D3859-A - Use independent reference material	(ASTM International, 2008)
GF-AAS	AWWA 3113B (Se only)	Dissolved: - Filter acid preserved sample (0.45 μm) - Add 3 mL H_2O_2 per 100 mL sample and $NiNO_3$ Total recoverable: - 100 mL sample, unfiltered - Add 1 mL HNO_3, 2 mL H_2O_2 - Heat until volume reaches 50 mL, cool - Add $NiNO_3$ and dilute to 100 mL with DIW	2 μg/L	No data	Accuracy and precision: - Se in waters at 10 μg/L: 6–12% error, 17–48%RSD (overall precision) - Se in effluent at 10 μg/L: 17–36% error, 30–51%RSD (overall precision) Demonstration of capability - Method detection limit - Linear dynamic range, Quality control: - ≥4 point calibration curve (including blank) - CCV at midpoint of calibration curve, 90–110% accuracy - CCB at the beginning, during and end of analysis - LCS - Matrix blank or reagent blank every 20 samples - LFB at midpoint of calibration curve, analyst to set criteria and record on control chart - Replicate sample analyzed each sample set - LFM and LFM duplicate every 20 samples - 10-Fold diluted sample value within 10% of original value	(Rice et al., 2012)
AV-ICP-OES	EPA 200.5 (multi-element)	Total recoverable: - 50 mL sample - Add 1 mL HNO_3 (50% v/v), 0.5 mL HCl (50% v/v) - Heat via block digester at 95 °C to volume of 25 mL, reflux 30 min, cool - Dilute to 25 mL with DIW	2 μg/L	2.9 μg/L	Accuracy and precision: - NIST SRM 1643 (12.7 μg/L) - Surface water, well water, tank storing water (Se < 2.9 μg/L): spiked at 50 μg/L, 95–104% recovery and 1.2–2% RSD - Well water (Se 4.1 μg/L): spiked at 50 μg/L: 100% recovery and 1.1% RSD	(U.S. EPA, 2003)

AV-ICP-OES	ISO 11885 (multi-element)	Direct analysis: - Sample must be colorless with turbidity <1.5 NTU Dissolved: - Filter acid preserved sample (0.45 µm) - Matrix match standards Total recoverable (aqua regia digestion): [From ISO 15587-1] - 25 mL sample (unfiltered) - Add 6 mL HCl and 2 mL HNO_3, - Heat 103 °C until no reaction occurred *Open digestion*: - Connect to reflux condenser - Reflux at least 2 h until digestion complete - Rinse condenser - Transfer to volumetric flask and dilute to 50 mL *Closed digestion*: - Cap vessel - Weight the vessel and sample - Microwave (autoclave alternative) at 103–175 °C at 101.3 kPa, - Digestion at least 10 min until complete digestion (max 480 min), - Cool - Weight vessel and make up to same weight Total recoverable (nitric acid digestion) [From ISO 15587-2] - 25 mL sample (unfiltered) - Add 6.25 mL HNO_3 - Heat at 103 °C until no reaction occurred - Perform open or closed digestion, as noted above for the nitric acid digest Suspended: - Use particulates collected on 0.45 µm filter from "dissolved" fraction - Add 4 mL HNO_3 and 4 mL H_2O_2, reflux - Add 3 mL HNO_3 and 3 mL H_2O_2 heat until digestion complete (evaporated to 2 mL), cool - Add 10 mL HCl, 15 mL DIW, warm, cool, and filter (0.45 µm)	No data	7 µg/L	Quality control: - IPC drift <10% - Independent calibration check 90–110% accuracy at the beginning and once every sample set - Reagent blank every 25 samples - Spike recoveries evaluated	(International Organization for Standardization, 2007) (International Organization for Standardization, 2002a) (International Organization for Standardization, 2002b)
USN-ICP-AES	EPA 200.15 (multi-element)	Direct analysis: - Sample must have turbidity <1 NTU (unfiltered, acid preserved) Dissolved:	8 µg/L	5 µg/L (direct analysis) 3 µg/L (total recoverable)	Accuracy and precision: - Tap water (from four water supplies): 94–119% spike recovery (50 µg/L) and 0.3–6.4% RSD - River water (one surface water): evaluate spike recovery	(U.S. EPA, 1994d)

Table 4 (*continued*)

Method	Standard method	Digestion method for each Se fraction	IDL-Se	MDL or LOQ-Se	Method performance indicators to be reported	Reference
					Demonstration of capability:	
		- Filter acid preserved sample (0.45 µm) - Add HNO₃, HCl and H₂O₂ to obtain 2%, 1% and 4%, respectively Total recoverable:			- Linearity dynamic range - QCS to verify calibration, 95–105% accuracy - MDL stated at 99% confidence level QC requirements:	
		- 100 mL acid preserved sample - Add 2 mL HNO₃ (50% v/v) and 1 mL HCl (50% v/v) - Heat at 85 °C, evaporate to 20 mL - Gently reflux for 30 min, cool - Add 0.2 mL H₂O₂ and make up 100 mL with DIW.			- LRB every 20 samples (LRB < MDL) - LFB analyzed between every sample set 85–115% accuracy - LFM (spiked at same level as LFB) analyzed between every sample set, 70–130% accuracy - IPC every 10 samples, 90–110% accuracy - CCB every 10 samples (CCB < IDL or within 99% confidence control limit of calibration blank) - Matrix spike recovery evaluation	
ICP-MS	EPA 200.8 (multi-element)	Direct analysis: - Sample must have turbidity <1 NTU (unfiltered, acid preserved) Dissolved: - Filter acid preserved sample (0.45 µm) - Add HNO₃ to achieve 1% acid. Total recoverable: - 100 mL acid preserved sample - Add 2 mL HNO₃ (50% v/v) and 1 mL HCl (50% v/v) - Heat at 85 °C, evaporate to 20 mL - Gently reflux for 30 min, cool and make up to 50 mL with DIW - Let stand overnight and filter (0.45 µm) if needed. - Add internal standard solution Total recoverable (high turbidity): - For samples with solid content >1% - Evaporate to 10 mL - Add 4 mL HNO₃ (50% v/v) and 10 mL HCl (25% v/v) - Reflux at 95 °C for 30 min, evaporate to 4 mL, cool and dilute to 100 mL with DI - Prior to analysis, take 20 mL and dilute to 100 mL	5 µg/L (scan mode) 1.3 µg/L (SIM mode)	7.9 µg/L scan mode and 0.5 µg/L SIM mode for direct analysis and 2.1 µg/L for total recovery	Accuracy and precision: - Reagent water bias; calculation for bias and precision as: $(Se_{cal}) = 1.022X + 0.14$, reproducibility $(S_R) = 0.056Se_{cal} + 2.10$ (where X is the determined concentration and S_R is the reproducibility) - Groundwater bias $(Se_{cal})_1 = 1.045X - 0.83$, $S_R = 0.091Se_{cal} + 2.03$ - Reagent water bias $(Se_{cal}) = 1.036X + 0.06$, $S_R = 0.051Se_{cal} + 3.24$ - Samples: 99–129.5% spike recovery (50 µg/L) and 1.8–10.9% RSD or as per equation (32–200 µg/L) Demonstration of capability: - Linear dynamic range - QCS to verify calibration, 90–110% accuracy - MDL stated at 99% confidence level QC requirements: - LRB every 20 samples (LRB < MDL) - LFB analyzed between every sample set, 85–115% accuracy - IPC every 10 samples, 90–110% accuracy - LFM (spiked at same level as LFB) analyzed between every sample set, 70–130% accuracy - Throughout analysis, internal standard response within 60–125% of the original response	(U.S. EPA, 1994c)
ICP-MS	ASTM D5673 (multi-element)	Dissolved: - Filter acid preserved sample (0.45 µm) - Add HNO₃ to achieve 1% v/v HNO₃ - Add internal standard Total recoverable:	5 µg/L	No data	Accuracy and precision: - See EPA 200.8 Demonstration of capability:	(ASTM International, 2016)

		- 100 mL acid preserved sample (unfiltered) - Add 2 mL HNO₃ (50% v/v), 1 mL HCl (50% v/v) - Heat, evaporate to 25 mL, cool, filter (0.45 μm), dilute to 100 mL with DIW			- IDL and MDL: spiked reagent water (n = 7) at 2xDL$_{estimated}$ and 5xDL$_{estimated}$ - Inter-laboratory comparison Quality control: - Cal curve: ≥3 points plus calibration blank - IPC analyzed between every sample set and at the end of analysis, 90–110% accuracy - CCB analyzed between every sample set and at the end of analysis, (accepted CCB < 2.2xMDL) - QCS analyzed between every sample set, 90–110% accuracy - Internal standard 65–125% of the original response	
ICP-MS	EPA 6020B (multi-element)	Dissolved: - Filter acid preserved sample (0.45 μm) - Adjust acid content to match standards Total recoverable (EPA 3005): - 100 mL acidified sample (unfiltered) - Add 2 mL HNO₃ and 5 mL HCl - Heat at 90–95 °C, evaporate to 20 mL - Cool, filter (0.45 μm) and dilute to 100 mL with DIW Total recoverable (EPA 3010) - 100 mL acidified sample (unfiltered) - Add 3 mL HNO₃ - Heat, evaporate to 5 mL, cool - Add 3 mL HNO₃, heat to gently reflux, add additional HNO₃ if necessary, evaporate to 3 mL - Cool, add HCl (50% v/v) to make 10% acid in final solution - Reflux for 15 min, cool, filter (0.45 μm) and dilute to 100 mL with DIW	No data	No data	Demonstration of capability: - IDL: n = 10 (reagent blank) - LLOQ: n = 7, 65–135% recovery, <20% RSD QC requirements: - Calibration curve ≥3 points plus calibration blank - Calibration blank <1/2 of LLOQ - ICV, 90–110% accuracy - Low level verification 80–120% accuracy - Mid-level verification 90–110% accuracy - CCV every 10 samples and at the end of analysis, 90–110% accuracy - Matrix blank (<LLOW) analyzed between every sample set - LCS or reference material every 20 samples, 80–120% recovery - Matrix spike, 75–125% recovery and matrix spike duplicate within 20% RPD - Internal standard not <30% of original signal - 5-Fold dilution of test solution within 20% of original value - Replicate sample analyzed every sample set	(U.S. EPA, 2014a) (U.S. EPA, 1992b) (U.S. EPA, 1992a)
ICP-MS	AWWA 3125 (multi-element)	Total recoverable: - 10 mL acid preserved sample - Add 0.5 mL HNO₃, heat at 105 °C for 2 h - Add more HNO₃, heat until solution is clear - Cool, dilute to 10 mL with DIW	0.064 μg/L	No data	Accuracy and precision: - Check spike recoveries for dissolved and total recoverable fractions Demonstration of capability - IDL, MDL and linear dynamic range Quality control: - Calibration curve >5 points, plus calibration blank - Calibration blank less than MDL - CVS at a midpoint of calibration curve, 90–110% accuracy - LFB or LCS at a midpoint of calibration curve, 70–130% recovery - Replicate samples, <20% RPD - Evaluation of NIST SRM 1643 or equivalent material - Matrix spike analyzed between every sample set, 75–125% recovery - Internal standard response 70–125% of original signal	(Rice et al., 2012)

Table 4 (*continued*)

Method	Standard method	Digestion method for each Se fraction	IDL-Se	MDL or LOQ-Se	Method performance indicators to be reported	Reference
ICP-MS	EPA 1638 (multi-element)	Dissolved: - Filter ≥20 mL acid preserved sample (0.45 μm) - Add HNO$_3$ to 1% v/v - Add internal standard(s) Total recoverable: 100 mL acid preserved sample (unfiltered) - Add 2 mL HNO$_3$ (50% v/v) and 1 mL HCl (50% v/v) - Heat to 85 °C, evaporate for 2 h (to 20 mL), reflux for 30 min - Cool, dilute to 50 mL, add internal standard Total recoverable (alternative): - Add 10 mL HNO$_3$ and 5 mL HCl per liter of sample - Cap the container and heat in an oven at 85 °C for 2 h - Cool, add internal standard	No data	1 μg/L	Demonstration capability: - MDL, linear calibration ranges - Spiked reagent water: 63–145% Recovery, 41% RSD - Quality control standards (standard solution from a different source) (n = 3) 90–110% accuracy Quality control: - CCV at midpoint of calibration, 69–127% accuracy - Matrix spike and matrix spike duplicate: 59–149% recovery, <20% RPD - LRB 59–149% recovery - One method blank and one equipment blank (bottle blank and equipment cleaning blank) per batch (<MDL)	(U.S. EPA, 1996a)
ICP-MS	AOAC 993.14 (multi-element)	Dissolved: - Filter acid preserved sample (0.45 μm) - Add HNO$_3$ to achieve 1% v/v Total recoverable: - 100 mL acid preserved sample (unfiltered) - Add 1 mL HNO$_3$ and 0.5 mL HCl - Heat, evaporate to 20 mL, reflux - Cool and dilute to 50 mL, pipette 20 mL and dilute to 50 mL	No data	7.9 μg/L	Accuracy and precision: - Reagent water, samples: 98.107.1% spike recovery (30–200 μg/L) 4.2–9.8% RSD - 100 μg/L standard solution: 79–128% recovery Demonstration of capability: - MDL - LFB Quality control: - QCS 100 μg/L = 79–128% recovery - LRB, CCB and rinse blank - LFB - QCS - Internal standard 60–125% of original response - CCV/10 analyses	(AOAC International, 1993)
ICP-MS	ISO 17294-2 (multi-element)	Total recoverable (aqua regia digestion): [From ISO 15587-1; see ISO 11885, above] Total recoverable (nitric acid digestion): [From ISO 15587-2; see ISO 11885, above]	No data	1 μg/L	Quality control: - Calibration blank ≤3xIDL - QCS 90–110% recovery - Spike recovery, 75–125% - Difference between results for the original sample and the fivefold-diluted sample ≤20%. - Internal standard solution 70–130% of original count - Interference check solution - Correction $^{82}Se = {}^{82}Se - 1.009(^{83}Kr)$ and ≤20% of uncorrected result	(International Organization for Standardization, 2016) (International Organization for Standardization, 2002a) (International Organization for Standardization, 2002b)

List of acronyms used in Table 4:
EDL: electro discharge lamp, STDEV: standard deviation, RSD: relative standard deviation, IPC: instrument performance check, CCB: continuing calibration blank, CCV: continuing calibration verification, LCS: laboratory control sample, LFM: laboratory fortified matrix, QCS: quality control sample, LRB: laboratory reagent blank, LFB: laboratory fortified blank, LLOQ: lower limit of quantification, MDL: method detection limit, IDL: instrumental detection limit.
[a] Unless otherwise noted, a "sample set" is considered to be 1 10th of an entire batch of samples.

3.3. European Union water quality guidelines

The EU established the water policy framework Directive 2000/60/EC and Directive 2008/105/EC to avoid long term deterioration of surface water, groundwater and marine water quality (The European Parliament and the Council of the Eurpoean Union, 2000, 2008). Se is only regulated under Directive 98/83/EEC on the quality of water intended for human consumption which controlled the maximum level at 10 μg/L (The European Parliament and the Council of the Eurpoean Union, 1998). This value is endorsed by EU members (e.g. Ireland, UK, Germany, Poland, Romania, and Bulgaria, as noted in Table 1). Another Directive that involves metals and their compounds is Directive 2006/118/EC (The European Parliament and the Council of the Eurpoean Union, 2006b); other priority substances regulated under EU water policy can be explored in Decision No. 2455/2001/EC (The European Parliament and the Council of the Eurpoean Union, 2001). Interestingly, Se is not specifically mentioned in this document, unlike Directive 80/68/EEC on the release of certain dangerous substances into groundwater and Directives 76/464/EEC and 2006/11/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment – regulations which are no longer enforced (The European Parliament and the Council of the Eurpoean Union, 1976, 1979, 2006a).

3.4. Asian water quality guidelines

The exposure of Se to humans (selenosis) was discovered in Enshi District, Hubei Province China between 1958 and 1963 and at the same time, 150 km away, Keshan disease (Se deficiency) was reported in Zhangjikou District, Hubei Province (Li et al., 2012; Yin et al., 2013). Clearly, soil chemistry plays an important role in the release of Se from different types of soil. Agricultural plants and livestock samples from Zhangjikou and Shadi, Enshi district were sampled and analyzed for Se concentrations and it was concluded that the major source of Se exposure to human was from food (rice, corn, vegetable, chicken and egg). Therefore the recommendation was to change daily diets and manage soils to increase Se uptake into plants in the Keshan disease-affected areas. Conversely, the trend of Se in agricultural plants in selenosis-affected areas decreased from 1963 to 2010, due to the loss of Se through natural volatilization (Johnson et al., 1996; Li et al., 2012). Another area in Asia where seleniferous soils have been reported is Northwestern India (Dhillon and Dhillon, 2014). There is little English information available relating to standards for Se in waters in Asia, though the drinking water standard in many Asian countries is set at 10 μg/L.

4. Analytical methods for selenium in waters used by U.S. regulatory bodies

This section will focus on the analytical methods for the determination of Se in waters used by U.S Federal Departments and will also discuss other "standard methods" that are recognized worldwide. These standard methods for water and wastewater analysis are published by highly respected scientific organizations, though they are not mandatory standard test methods based on any official legislation. However, the local regulatory authority under the Nation Acts has endorsed and approved the standard methods for nationwide or regional use.

4.1. Selenium determination by gravimetric methods

Following Swedish scientist Jacob Berzelius' initial discovery of Se in 1818 (Trofast, 2011), he collaborated with Heinrich Rose to develop the first method for the quantitative analysis of Se based on a gravimetric method (László Erdey et al., 1965). Later, a similar concept of gravimetric measurement was developed, but with titration to quantify Se in seleniferous materials and geological samples (Dudley and Byers, 1934;

Norris and Fay, 1896; Noyes and Bray, 1924; Scott, 1917). AOAC International (unofficially, the "Association of Analytical Communities") modified these two methods to analyze Se in biological samples as method "AOAC 936.04 - Se in plants", and "AOAC method 939.09 - Se in food" (Horwitz, 2000; Robinson et al., 1934). The sample preparation to separate Se from the sample matrix was modified for Se determination in water by the USGS in 1960 (Rainwater and Thatcher, 1960).

For this analysis, Se is oxidised by hydrogen peroxide, sulfuric and nitric acid, then reduced to H_2SeO_4 with hydrogen bromide-bromine to liberate Se tetra-bromide in a distillate. The collected distillate is then reduced by hydroxylamine hydrochloride or sodium bisulfite and oven dried to precipitate Se for quantification by weighing. This technique is not appropriate for Se concentrations <1 mg/kg. The quantitative analysis of Se in water can be achieved by the precipitation of elemental Se^0 in a gum arabic solution and matching the colour against standard Se solutions (Robinson et al., 1934).

4.2. Selenium determination by visual colorimetric comparison

The colorimetric comparison of elemental Se suspensions was first used by the U.S. PHS in 1946. At the time, Se was regulated at a maximum level of 50 μg/L (World Health Organization, 1958), and the gravimetric method was not sufficient to measure Se at the low concentrations present in drinking water. Therefore, the method of analysis for Se was modified to use a colorimetric comparison. The sample is prepared in the same way as the gravimetric method, mentioned above. The distillate is collected in hydrogen bromide-bromine solution. The fine pink to red Se particulate can be observed after the colour interference of bromine is removed. The pink particles are suspended in the solution of gum arabic in a Nessler tube and ready for visual colour matching against Se standard solution. The visual colour comparison was claimed to be able to detect Se present in concentration from 5 to 10 μg/L. The colorimetric comparison appeared in the Standard test methods for the examination of water, sewage and industrial wastes (American Public Health Association (APHA), 1955) and WHO during the period from 1958 to 1971 (World Health Organization, 1958, 1963, 1971). The disadvantages of this method include the fact that it requires a large amount of sample (up to 10 L), the long time required for the distillation process, and the toxicity of the bromine solution.

4.3. Selenium determination by titration

Improved analysis of Se was achieved by titrimetric method. Following distillation and Se precipitation, as described above, the Se particles are re-dissolved with hydrogen bromide bromine solution to form H_2SeO_3 and an excess of 0.001 N sodium thiosulfate is added. The solution is then back titrated with a standard iodine solution using a starch solution as the indicator. The back titration is calculated as 1.00 mL of 0.001 N sodium thiosulfate being equivalent to 0.0198 mg of Se. This method can provide a low detection limits for Se when using larger volumes of water (maximum of 100 mL) containing Se in amounts <0.5 mg. With careful work, results are accurate and reproducible to ±0.002 mg. Potential sources of interference include the presence of oxidizing compounds in solution. This titration of Se with excess sodium thiosulfate is known as Norris-Fay titration and has been used since 1896 (Coleman and McCrosky, 1937). The quantitative analysis of Se using distillation and titration appeared in "Methods for Collection and Analysis of Water Samples" published by the USGS in 1960 as method D:33a-1: Norris-Fay Titration Method, which was modified from the Association of Official Agricultural Chemists in 1945 (Rainwater and Thatcher, 1960).

4.4. Selenium determination by colorimetry (spectrophotometry)

A spot test for Se was first developed for qualitative purposes, using the redox reaction of H_2SeO_3 with reducing agents (hydriodic acid or

thiourea). Se^0 obtained from this step is further reacted with sulfuric acid to form a blue coloured complex with codeine. This method was used for biological samples and good results were achieved at concentrations above 1 mg/kg. The colorimetric-basis of this complexing method gave it the potential for development into a quantitative method (Frank et al., 1936; Horn, 1934; Stahl, 1969).

In 1962, the American Water Works Association (AWWA)/American Public Health Association (APHA), joint committee considered a new method proposed for the determination Se in water by colorimetry using 3,3 diaminobenzidine as a complexing agent. Here, following sample digestion, complexation is completed under alkaline conditions and the resulting red-coloured 5,5 dipiazselenol is extracted into an organic phase (typically toluene) for spectroscopic measurement against a standard solution which is prepared in the same manner. However, other metals interfere with this complexation, and must be removed through chelation with ethylenediamine tetra-acetic acid (EDTA) to ensure accurate Se analysis (U.S. EPA, 1971b). It should be noted that 3,3 diaminobenzidine is carcinogen and therefore stringent regulations are in place regarding its commercial availability.

The tested method and results of Se concentrations in waters from a collaborative study had been proposed by the AWWA/APHA. There was an agreement in results among the participating laboratories with accurate and precise data (AWWA Editorial Board, 1963; Skougstad and Fishman, 1963). This method replaced the visual colour comparison method and was published in "Standard Method of Analysis in Water and Wastes" by APHA, 12nd Edition in 1965. This method was used for Se in surface water by the U.S. Federal Water Pollution Control Administration in 1968 (Federal Water Pollution Control Administration, 1968; U.S. EPA, 1971a). The USGS also endorsed this method in "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases" in 1970 (Brown et al., 1970). This colorimetric method with 3,3 diaminobenzidine was able to detect as little as 10 μg Se using wavelength 420 nm.

U.S. Federal Water Pollution Control and USGS had specified the terms "dissolved Se", "suspended Se", and "total Se" in their test reports. Dissolved Se is obtained when the sample is filtered through a 0.45 μm membrane prior to analysis, total Se is the amount present in the water without filtration, and suspended Se is the difference between the first two measurements (Federal Water Pollution Control Administration, 1968; Wallschläger and Roehl, 2001). At present, the determination of Se can be specified as "dissolved Se" and "total recoverable Se".

Alternatively, other complexing agents such as 2,3 Diaminonaphthalene (DAN) can be used and produce brightly coloured and strongly fluorescent piazselenol compounds which can be measured at 480 nm with detection limits around 10 μg/L. The DAN colorimetric method for Se appeared in APHA-Standard Method, 22nd Edition in 2012 as Standard Method 3500-Se(C) (Rice et al., 2012). The development of new complexing agents is still an active field of research (Krishnaiah et al., 2003; Narayana and Mathew, 2006; Soruraddin et al., 2011). Commercial test kits for the determination of Se in water based on this type of chemistry are capable of detecting Se in the 0.01 to 1.0 mg/L range when used with a 1 cm absorption cell (Xu et al., 1997).

4.5. Selenium determination by fluorometry

Similar to the 3,3 diaminobezidine colorimetric method for Se analysis, a fluorescent complexing agent, 2,3 diaminonaphthalene (DAN), was developed and provides better sensitivity than conventional colorimetric reagents. The distillation process for sample preparation is omitted in these procedures, making this method significantly faster. However, DAN does need to be prepared freshly prior to analysis due to its sensitivity to air and light. Similarly, the use of EDTA is often required to complex metals which interfere with Se complexation.

For this method, the sample is acid digested with strong acid and reduced to H_2SeO_3 by hydrochloric acid. EDTA is added to mask interfering metals (tellurium, copper, zinc and aluminum) and the DAN solution is added. The 4,5 benzopiazselenol formed through this reaction is extracted into toluene, hexane, decahydronaphthalene, or cyclohexane (cyclohexane is recommended due to its low background interference). The colour of 4,5 benzopiazselenol depends on pH, reaction time and light conditions. The measurement is done at an excitation wavelength of 375 nm and a fluorescent emission wavelength of 525 nm (Lott et al., 1963). The fluorometric method had been used for Se in geological surveys of waters by the U.S. Water Research Institute and claimed to be able to analyze Se at concentration as low as 1 μg/L (Stach, 1978).

4.6. Selenium by hydride generation – atomic absorption spectrometry

It has long been known that distinctive colours are produced when compounds of certain metals are vaporized in flames. Since 1955, flame atomic absorption spectrometry (FAAS) has taken advantage of this phenomenon and has been widely used for the quantitative analysis of many elements; however, it is still not suitable for metalloids including Se (L'Vov, 1961; Walsh, 1955). Direct measurement of Se by FAAS is not recommended because the absorption line of Se at 196 nm is interfered by hydrocarbon molecules generated from air-acetylene in the flame. Other types of gas (i.e. propane-air, argon-hydrogen and nitrogen-hydrogen) have been studied to reduce the spectral absorption of hydrocarbons below 200 nm. Moreover, increasing the intensity of the light source by using an electrodeless discharge lamp was examined, but the detection limit of 200 μg/L was not suitable for the analysis of Se in most natural waters (Thompson and Thomerson, 1974; Winefordner and Vickers, 1972).

Due to the limited sensitivity for metalloids (Se, As, Hg) analysis by hydride generation (HG) FAAS has been developed. HG for Se involves two reducing steps: first reducing Se(VI) in digested solutions to Se (IV) using hydrochloric acid, stannous chloride, potassium/sodium iodide, or potassium bromide. The second step involves the reduction of Se(IV) to Se^{-2} using zinc powder, or magnesium or sodium borohydride in acidic solution to form volatile selenides (typically H_2Se). HG is widely used for the analysis of Se in waters due to its sensitivity, specificity, and affordability; therefore, the research on reducing reagents to increase the efficiency of hydride formation are still active and recently there has been a trend to move from inorganic to organic reducing agents (Limchoowong et al., 2015; Musil and Matoušek, 2008; Welz and Šucmanová, 1993; Yamamoto and Kumamaru, 1976).

The HG reaction is prepared by batch or continuous (flow injection) systems. Samples must be digested to ensure that all Se is present as inorganic species before proceeding with the two reduction steps mentioned above. Later, H_2Se is purged into a quartz tube placed on a furnace or burner and atomized by flame or flameless AAS. The measurement is taken as a transient signal and quantified by peak height or integrated peak area. The method of batch HG has the advantage of being able to handle large sample volumes (up to 100 mL), but it is time consuming to reach the equilibrium required for hydride reaction and diffusion to the flame. Continuous flow injection HG coupled to AAS (FI-HG-AAS) was developed with automated systems, reducing time, and improving precision; however, these methods are rather expensive (Chan and Sadana, 1992; Limchoowong et al., 2015; Piston and Knochen, 2012).

In 1974, the utilization of batch HG-AAS for Se analysis was issued by the U.S. EPA as Method 270.3 for dissolved, suspended, and total Se in drinking water, freshwater, and marine waters and the USGS published a HG-AAS protocol for total Se analysis as Method number I-3667-85 for batch HG-AAS and FI-HG-AAS (Fishman and Friedman, 1989; U.S. EPA, 1983). The USGS used the HG-AAS technique for a Se survey of selected streams in regions with mineable coal reserves in Eastern Kentucky in 1980; at the time, Se in waters was regulated at 5 μg/L. Most of the water samples from the sampling sites were reported at 0–2 μg/L (detection limit was 1 μg/L); only two samples were found to contain

higher concentrations of Se, at 5 and 6 µg/L (Downing-Kunz et al., 2005). HG-AAS for Se analysis appeared in APHA-Standard Method 301A in 1975, which later became Standard Methods 3114B (manual HG-AAS) and 3114C (continuous HG-AAS) (Rand et al., 1976; Rice et al., 2012). The capability to detect Se by HG-AAS below 1 µg/L was reported with sample volumes of 50–100 mL for batch systems (Fishman and Friedman, 1989; International Organization for Standardization, 2013).

The current version of WHO-Guidelines for Drinking Water Quality references HG-AAS for Se analysis. U.S EPA 40 CFR 136 (Clean Act Water) and 40 CFR 141 (Safe Drinking Water Act) have approved mandatory methods for Se analysis by HG as follows: APHA-Standard Method 3114B, 3114C, ASTM D3859-A and USGS Method I-3667-85. The USGS Method 1-3667-85 is not mentioned for Se analysis in drinking water by 40CFR 141 (ASTM International, 2008; U.S. EPA, 2017a, 2017c, 2017e). However, there is a concern based on the sample preparation by acid digestion using perchloric acid, which is not recommended by the U.S. EPA because of its potential danger (U.S. EPA, 1994a, 1994b, 1994c).

4.7. Selenium determination by graphite furnace atomic absorption spectrometry

Graphite furnace (GF)-AAS, also known as electro-thermal atomization (ETA)-AAS, electro-thermal vaporization (ETV)-AAS, or flameless AAS, was developed at the same time as FAAS. GF-AAS affords the determination of most metallic elements with a smaller amount of sample consumed (10–50 µL), excellent sensitivities and detection limits, and direct analysis without sample preparation. However, the disadvantage is the cost of GF-AAS itself, which includes the consumption of a graphite tube and additional inert gas, typically argon/nitrogen (Ashino et al., 2010). However, an important advantage of GF-AAS over FAAS is that GF-AAS can analyze metalloid species with satisfactory sensitivity.

As the GF-AAS is working with a transient signal, the use of a modifier to assist pyrolysis/atomization, a temperature program, and purging gas maintain the retention time of atom vapor to enhance the absorption and to remove spectral interferences (e.g. iron, chloride, sulfate). The graphite tube has been specifically designed in terms of its shape as well as through the development of a pyrolytic coating material to assist in temperature homogeneity during atomization and to expand a lifetime of the graphite tube under high temperatures in corrosive solutions (Moreira et al., 2007). The use of background correction (i.e. Zeeman or Deuterium background correction) to overcome the matrix spectral interferences can significantly increase the capability of GF-AAS to determine metal contaminants in low the µg/L range. For Se analysis, the interferences in water samples include chloride, sulfate, sodium and potassium. Palladium nitrate or nickel nitrate modifiers are preferred. The detection limit of Se by GF-AAS has been published recently at <1 µg/L (Greenberg et al., 1992; Hergenreder; Niedzielski and Siepak, 2003).

A GF-AAS technique was first issued by the U.S. EPA in 1969 under "atomic absorption methods" and in 1978 became Method 270.2 for dissolved, suspended and total Se analysis in water and waste. A detection limit of 2 µg/L was reported for Se and the method remained in effect until 1996 (U.S. EPA, 1983, 1994). Later, the U.S. EPA revised methods for all elements, including Se, by GF-AAS and the analysis of 15 trace elements together became EPA Method 200.9. This EPA Method specifies the type of graphite platform to be used as a stabilised temperature graphite platform or a transverse heated graphite platform (U.S. EPA, 1994a).

In 1985, the determination of Se by GF-AAS appeared as APHA-Standard Method 304 (Greenberg et al., 1985) which was later revised to Standard Method 3113B and is still active in the current version published in 2017 (Rand et al., 1976; Rice et al., 2012). The use of GF-AAS for Se analysis in water has been seen in the USGS as Method I-2668-98 with a method detection limit of 1 µg/L for Se (Jones and Garbarino, 1998). The USGS recommended the use of a GF-AAS instrument which has a Zeeman background correction system and transverse heated graphite atomizer (THGA) and is capable of achieving detection limits of 1 µg/L. Methods for GF-AAS analysis of Se in water are also published in ASTM D3859-B and ASTM D3919, but in ASTM D3919 it is only mentioned as a general practice of GF-AAS for trace elements analysis including Se (ASTM International, 2004, 2008).

U.S EPA 40 CFR 141 (Safe Drinking Water Act) has approved test methods for Se from EPA 200.9, ASTM D3859-B and APHA 3113B, while EPA 40 CFR 136 (Clean Act Water) accepts only EPA 200.9 (U.S. EPA, 2017a, 2017c).

4.8. Selenium by inductively-coupled plasma atomic emission spectrometry

The simultaneous multi-elemental nature of inductively-coupled plasma atomic emission spectrometry (ICP-AES), which is also known as ICP optical emission spectrometry (ICP-OES), has clear advantages over AAS-based methods for multi-element analysis, with a large dynamic linear range and refractory element removal in the high-temperature plasma. ICP-AES was introduced to the U.S. EPA in order to improve instrumentation for identification and quantification of environmental pollutants. Using the prominent lines of the ICP emission of 70 elements, each spectral line of elements was studied by the Ames Laboratory under the sponsorship of the U.S. EPA from 1977 to 1978. For Se, the spectral lines were reported at 196.026, 203.985, 206.279, 207.479 and 199.511 nm, noted here in order from highest to lowest sensitivity. The estimated detection limit using the 196.026 nm line (as is generally used for Se analysis) was calculated to be 75 µg/L (Winge et al., 1979). The U.S. EPA method for the analysis of 33 elements in water and wastes by ICP-AES was published in 1982 as a new method called Method 200.7 and it is still active in the current version of the guide (U.S. EPA, 2015). However, with typical ICP-AES, the detection limit for Se raises questions of whether the method can be used to analyze the concentrations below 10 µg/L present in drinking water. The development of an ultrasonic nebulizer (USN) to obtain a larger amount of fine aerosol was published in EPA Report-600/R-94/111 in 1994 as method 200.15 (U.S. EPA, 1994d). The detection limit for Se using USN-ICP-AES decreased significantly to below 8 µg/L from 75 µg/L using a conventional pneumatic nebulizer (International Organization for Standardization, 2007).

The criteria of ICP-AES instrumentation in EPA Method 200.7 only specifies a general ICP-AES system with background-correction, meanwhile EPA Method 200.15 added "Section 6.1.5 UNS - A radio-frequency powered oscillating transducer plate capable of providing a densely populated, extremely fine desolvated aerosol" (U.S. EPA, 1994d). However, the sensitivity for some elements, including Se, by ICP-AES was still not adequate for natural water analysis. The idea of axially viewed (AV) ICP-AES was introduced to the U.S. EPA for multi-elemental analysis because of its improved sensitivity. The changing of the torch position and viewpoint configuration of the spectrometer from radially to axially provided larger emission signals and more stability during the entire measurement process (U.S. EPA, 2003).

Nobrega et al. (2002) evaluated the performance of ICP-AES between axially and radially viewed configurations and observed that an ICP-AES axial configuration can increase sensitivity 20–30 times for Se analysis. The study demonstrated detection limits ranging from of 4 to 6 µg/L in waters with varying carbon content. Meanwhile, EPA Method 200.5 (Determination of trace elements in drinking water by AV-ICP-OES) claimed a detection limit of 2 µg/L for Se (U.S. EPA, 2003). Some AV-ICP-AES instruments are configured such that the emitted signal can be viewed alternately or simultaneously in a radial manner, called "dual view ICP" in which the user can obtain both sets of results in a single analysis. Therefore, the radially viewed signals can be used for the determination of major matrix elements such as Ca, Mg, Na, and silica. EPA Methods 200.5 (using AV-ICP-AES) and 200.7 (ICP-AES) are accepted for Se analysis in the Clean Water Act (U.S. EPA, 2018a).

However, for drinking water, EPA Method 200.5 is accepted as an alternative test method (U.S. EPA, 2018b), whereas EPA Methods 200.7 and 200.15 are not referred to as accepted methods for Se analysis in drinking water (U.S. EPA, 2018c).

An ICP-AES method for multi-elemental analysis, including Se, is also published in ISO 11885–2007; the detection limits for Se at 196.026 and 203.985 nm are stated to be 100 µg/L for radial viewing and 2 µg/L for axial viewing. The UNS is also possible for the analysis of selenium in water samples in the low concentration range (International Organization for Standardization, 2007). An ICP-AES method is also published in APHA Method 3120B (Greenberg et al., 1992) and ASTM D1976 (ASTM International, 2012b).

4.9. Selenium analysis by inductively-coupled plasma mass spectrometry

Mass spectrometry (MS) has become widely used by researchers as a powerful tool for analytical chemistry. ICP-MS is able to analyze a most elements in the ppt (ng/L) to ppb (µg/L) range and can be applied to higher precision measurements through the application of isotope dilution mass spectrometry (IDMS), which is discussed in further detail in the next section. The advantage of its sensitivity makes ICP-MS is applicable to the analysis of ultra-trace elements in natural waters. While single quadrupole-ICP-MS is by far the most commonly used, the presence of isobaric interferences on the masses of Se isotopes present some challenges.

Se has naturally-occurring stable isotopes at masses 74, 76, 77, 78, 80 and 82 amu. In the high temperature plasma, argon (Ar) becomes ionized and forms positively charged polyatomic ions ($^{40}Ar_2^+$, $^{38}Ar_2^+$) and also with other matrix elements such as chlorine, sulfur, nitrogen, and calcium, all of which interfere with various Se isotopes (see Table 2). Further interference arises from elements which have the same isotope as Se, such as krypton, which is a common impurity in argon. Table 2 shows isotope interfering Se analysis (De Bièvre and Barnes, 1985; May and Wiedmeyer, 1998).

Some isobaric interference, such as ^{82}Kr, can be removed using background subtraction. A mathematical correction model (Eq. (2)) is recommend by APHA Method 3125 and ISO 17294-1 (Rice et al., 2012; Wiel, 2003). However the U.S. EPA Method 200.8 does not specify the correction factor for ^{82}Kr, but stated that if the correction factor is used then a record of this correction process should be included in the report of the data. The correction factor is dependent on the accuracy of isotope abundance used for calculation (U.S. EPA, 1994c).

$$^{82}Se = {}^{82}C - (1.008696 \times {}^{83}C) \tag{2}$$

where C is the calibrated blank-corrected counts at indicated masses, and

$$1.008696 = \frac{Abundance\ of\ {}^{82}Kr}{Abundance\ of\ {}^{83}Kr} = \frac{11.6}{11.5}{}^{**}$$

**1.008696 is derived using isotope abundance from spectroscopyonline.com (Neubauer, 2010; Rice et al., 2012).

However, this type of mathematical correction model does not work when the signal from the interference is higher than that of the analyte. Instead, advanced technologies using a collision reaction cell (CRC) or dynamic reaction cell (DRC) have been developed to eliminate these types of interferences (Koppenaal et al., 2004; Rottmann et al., 2012; Salazar et al., 2011; Tanner and Baranov, 1999). These reaction cells operate as rf-only multipoles, situated before the mass analyzer, which can be pressurized with a gas to induce various ion-molecule reactions in one of two scenarios. In the first, a gas is chosen to react with the analyte ions, changing the mass and allowing for detection without interference; for example, O_2 gas can react with ion X^+ to form XO^+ which can then be monitored at mass $x + 16$. Alternately, the cell gas can

react with the interference to change its mass, allowing the analyte ion to be measured at its native *m/z*. The latter scenario is more commonly employed for Se, for example CH_4 will react with $^{40}Ar_2^+$ allowing for the analysis of ^{80}Se (Tanner et al., 2002). The application of collision and reaction cells in ICP-MS significantly lowered detection limits for difficult-to-analyze elements such as Se, where even in the early days of the technology detection limits in the low- or sub-ng/L range were obtained (Sloth and Larsen, 2000; Tanner et al., 2000).

More recently, further advancements in ICP-MS technology have resulted in the production of triple quadrupole ICP-MS (ICP-QQQ-MS) instruments, first introduced by Agilent Technologies in 2012 (Kuwabara et al., 2012). Their design and operation is similar to collision/reaction cell instruments, but there is a mass analyzer both before and after the collision cell, allowing for extreme selectivity and elimination of most interferences. The application of ICP-QQQ-MS is especially beneficial for samples containing relatively high concentrations of interfering components in the matrix, as is frequently the case in contaminated waters.

Since 1990, a method for multi-element analysis by ICP-MS has been published as U.S. EPA Method 200.8 (U.S. EPA, 1994c). Other ICP-MS methods that have been approved for Se determination in clean water include APHA 3125B, ASTM D5673, AOAC 993.14, and USGS Method I-4020-05. An ICP-MS method (EPA Method 200.8) for Se determination in drinking water is also mentioned in the National Primary Drinking Water Act (40 CFR 141.23) Appendix A to Subpart C (U.S. EPA, 2017c). International Food Standards CODEX STAN 108-1981 suggest several methods for Se analysis in natural mineral waters (maximum level of 10 µg/L); including ICP-MS methods ISO 17294-2 and EPA 200.8 (Codex Alimentarius, 1999).

4.10. Selenium determination by isotope dilution mass spectrometry

IDMS represents the state-of-the-art in analytical chemistry and can be applied to both total element and speciation analysis. The method requires mass spectrometric measurements of the ratio abundance of two or more stable (or long-lived) isotopes of a given analyte and is based on the addition of a known amount of enriched isotope spike into a sample (Heumann, 1982, 1992). While sometimes rather expensive, these enriched isotope standards are commercially available, for example from LGC-UK and American Elements®, etc. Based on the measured ratios between the spiked isotope and a reference isotope in a sample and knowledge of the enrichment of the spike and the exact amount used, the concentration of analyte in the sample can be calculated as shown in Eq. (3).

$$C_x = C_y \cdot \frac{m_y}{m_x} \cdot \frac{A_y - B_y \cdot R_n}{B_x \cdot R_n - A_x} \cdot \frac{M_x}{M_y} - C_b \tag{3}$$

where:

C_x is the concentration of analyte in the sample,
C_y is the concentration of the analyte in the spike solution,
m_y is the mass of the spike solution used in the spike/sample mixture,
m_x is the mass of the sample,
A_y is the abundance of the reference isotope in the spike solution,
B_y is the abundance of the spike isotope in the spike solution,
A_x is the abundance of the reference isotope in the sample,
B_x is the abundance of the spike isotope in the sample,
R_n is the reference/spike isotope ratio in the spike/sample mixture,
M_x is the atomic weight of the reference isotope,
M_y is the atomic weight of the spike isotope,
C_b is the concentration of the analyte in the blank

One of the greatest advantages of IDMS is its high level of accuracy and precision due to its ability to account for analyte losses and/or changes during sample preparation because factors affecting the native analyte will affect the spike to an equal degree.

An important factor in the accuracy of IDMS measurements is the mass resolution achieved by the instrument; there are a variety of types of mass spectrometers, each with different capabilities. For the analysis of metal(loid)s, there are five basic types of ICP-MS instruments: single quadrupole (SQ-ICP-MS, which may contain a CRC or DRC), triple quadrupole (ICP-QQQ-MS), time of flight (ICP-TOF-MS), and sector field (magnetic and electric) instruments which may contain single collector, or multi-collector (MC-ICP-MS) detection systems.

A report on the analysis of Se in groundwater, river water and lakes samples by IDMS was published in 1991 by Heumann et al. using a Negative Thermal Ionization Mass Spectrometer (NTI-MS) measuring ratio of enriched ^{82}Se isotope and most abundant isotope ^{80}Se. Total Se was reported from 0.2 to 15.6 μg/L where Se(VI) was the major species (Tanzer and Heumann, 1990).

The U.S. EPA, under the Clean Water Act and National Primary Drinking Water Regulation, does not require IDMS for the analysis of any metal, including Se. However, IDMS method is recommended by the U.S. EPA for evaluating of solid wastes (known as SW-846) to comply with the Resource Conservation and Recovery Act (RCRA). EPA Method 6800 covers 20 elements, including Se, all of which have more than one isotope (U.S. EPA, 2014b; Vogl and Pritzkow, 2010).

5. Method requirements for selenium analysis in waters

5.1. Sample collection

Similar approaches for sample collection are described in U.S. EPA-600/4-82-029 (general sampling) and ISO 5667-3 (International Organization for Standardization, 2012; U.S. EPA, 1982); both of which are used as a general sampling guideline for a variety analytes in waters. AWWA Section 3010-B and EPA Method 1669 are related to sampling for metals analysis. EPA Method 1696 covers 13 metals (including Se) to comply with clean water regulations as these metals are regulated at very low concentrations (ng/L to μg/L levels). This standard has a stringent measure to control contamination generated from sampling, transportation, and analysis (Greenberg et al., 1985; U.S. EPA, 1996b). Water samples can be collected in a container made of quartz, borosilicate glass, propylene (PP), high density polyethylene (HDPE), fluoroethylenepolymer (FEP), polycarbonate (PC), or polytetrafluoroethylene (PTFE). The container needs to be washed with detergent, cleaned, rinsed with nitric acid (from 20 to 50% v/v) or mixture of nitric and hydrochloric acid, and soaked in or filled with dilute nitric or hydrochloric acid for at least 24 h before being rinsed with ultrapure water. When sampling, water samples must be filtered through (at least) 0.45 μm membrane filters (polycarbonate or cellulose esters) immediately upon collection. The container is completely filled with sample, without headspace, and kept as cool as possible after collection. It has been noted that exposure of a sample to air during filtration can cause co-precipitation of Se with iron and manganese oxide (Wu and Pichler, 2015).

5.2. Sample preservation

The purpose of preservation is to maintain the integrity of a sample, through the prevention of interactions with microorganisms, the reduction of co-precipitation and complexation of the analyte of interest and other matrix components, and to minimize adsorption of the analyte onto the sample container's surface. For (total) metals analysis, a water sample is typically preserved in nitric acid to achieve a final pH <2 (Rice et al., 2012; U.S. EPA, 1996b). However nitric acid preservation has caused difficulty when the subsequent analysis is performed via a reaction with sodium borohydride as the nitric acid can diminish the Se hydride signal (Campbell, 1992).

There is no standard method detailing guidelines for sample storage for the preservation of Se speciation; however, EPA Method 1632 discusses the preservation of arsenic species in water, during which hydrochloric acid is added and the recommended maximum storage time to preserve speciation is 28 days at 0–4 °C (U.S. EPA, 1998). Conversely, Se species are not stable in the presence of microorganisms or reducing or oxidizing compounds, therefore immediate analysis is generally recommended (Eswayah et al., 2016). There are several studies examining various storage conditions for Se species in waters (Héninger et al., 1997; Wiedmeyer and May, 1993; Wu and Pichler, 2015). For example, Wu and Pichler (2015) found that the speciation was preserved for small concentrations of Se (5 to 15 μg/L), in the presence of high concentrations of iron and manganese, through the addition of 0.5 M EDTA when the samples were stored in PE bottles at 4 °C in the dark for up to 11 weeks.

5.3. Sample preparation and quality control

Many standard methods of analysis have been discussed in this section. In these methods, sample preparation for Se and other metals is categorized based on three pools: dissolved, suspended, and total recoverable metals. AWWA section 3010 (A) adds an additional group – acid-extractable metals – and associated methods are applied to extract Se from suspended particulates and solid samples. The analysis of Se in waters is typically reported in two pools: dissolved Se and total recoverable Se (Rice et al., 2012).

Direct analysis of water samples is fairly uncommon and is only recommended for drinking water analysis where turbidity is <1 NTU (U.S. EPA, 2015). The dissolved fraction is defined as the amount of Se recovered after filtration a 0.45 μm membrane. Lastly, total recoverable Se measures all of the analyte in a sample for acid preserved waters and samples analyzed after acid digestion. Total recovery digestions typically acid use either nitric acid or aqua regia and can be conducted under closed (microwave or autoclave) or open (hot block, water bath, or hot block) conditions. For USN-ICP methods, hydrogen peroxide is added during digestion to enhance aerosol capability.

To ensure the integrity of acquired data, various quality control measures are implemented during sample collection, preparation, and analysis. These quality control measures are stated with acceptance criteria for various standard methods and include:

1. Maintenance of data generated from analysis
2. Demonstration of laboratory capability and proficiency participation
3. Routine quality control
   a. Multi-point calibration using standard solutions
   b. Analysis of a variety of types of blanks (field blank, rinsed/equipment blank, calibration blank, reagent/method blank)
   c. Accuracy and precision
      i. Lower limit of quantification measurement
      ii. Internal standardization
      iii. Recovery check using LFB, LFM, LCS, and/or CRM
      iv. Repeatability (duplicate samples, and duplicate spike fortified samples)
      v. Interval checks of system stability using continuing calibrations blanks, continuing calibration verifications (at a mid-point concentration)

The use of specific reference materials are not stated in any standard methods, and can therefore be chosen based on availability. There is a wide variety of water samples available as certified reference materials for total metals, but many are not certified for Se. Table 3 provides some examples of waters certified for total Se which are currently (as of writing date) available for purchase. Table 4 provides a list of standard methods which are widely used for routine analysis of total Se.

6. Conclusions

6.1. Limitations of total selenium analysis

Over the last few decades, methods for Se analysis have improved significantly in terms of their ability to quantify trace concentrations in natural and industrial waters. With regulations becoming increasingly strict, there is a need for analytical methods capable of accurately analyzing sub-μg/L concentrations of Se in the presence of interfering matrix components. While some standard methods can handle this, others demonstrate detection limits near or above the allowable concentrations of Se in many types of waters, making it extremely difficult to properly monitor these waters for potential toxicity. It is important to keep detection limit-based restrictions in mind when selecting analytical methods for testing environmental waters, and note that in the near future it may be necessary to move towards more sensitive and robust techniques for Se analysis. There are many review publications on the analysis of Se in waters by instrument modification to achieve better sensitivity (Pettine et al., 2015) or by using fractionation to preconcentrate and extract Se from interferences as detailed in Part 2 (LeBlanc et al., 2018). However the modified method has to meet performance criteria for the applied method of analysis, which are limit of detection, limit of quantification, accuracy, precision, and comparable studies (U.S. EPA, 2017b).

6.2. Speciation analysis

In this review (Part 1), the analysis methods discussed have all aimed to quantify the total concentration of Se in a sample, sometimes distinguishing between total recoverable, dissolved and suspended Se, but we have not examined the quantitative methods for analyzing discrete species of Se present in said samples. Se speciation can have a significant effect on the overall toxicity of the element in an ecosystem. In freshwater systems, algal uptake (and therefore incorporation into the food chain) of Se(VI) occurs to a greater extent than uptakes of Se(IV), though the opposite is true in saline waters (Baines and Fisher, 2011; Maher et al., 2010). Additionally, algal uptake of the organic Se species SeMet is significantly greater than that of either Se oxyanion (Riedel et al., 1991; Sandholm et al., 1973), meaning its presence in a water body could significantly alter the bioavailability of Se in that system. Therefore, to begin to have a thorough understanding of the potential for Se toxicity in an aquatic environment, it is essential to know the speciation of Se within that water body and to be able to account for species present even at small fractions of the total Se concentration. In Part 2 (LeBlanc et al., 2018), we continue the discussion of Se in aquatic ecosystems, looking at the state of speciation analysis through the examination of various analytical methods to quantify discrete Se species in waters. Additionally, we discuss the importance of speciation data for decision makers in industry and regulators.

Acknowledgements

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